

Environmental Protection Agency

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Citation	Requirement	Applies to subpart HHHH	Explanation
§ 63.9(f) .....	Notification of Visible Emissions/Opacity Test.	No .....	Subpart HHHH does not specify opacity or visible emission standards.
§ 63.9(g)(1) .....	Additional CMS Notifications .....	Yes.	
§ 63.9(g)(2)–(3) .....	.....	No .....	Subpart HHHH does not require the use of COMS or CEMS.
§ 63.9(h)(1)–(3) .....	Notification of Compliance Status.	Yes .....	§ 63.3000(b) specifies additional requirements.
§ 63.9(h)(4) .....	.....	No .....	[Reserved].
§ 63.9(h)(5)–(6) .....	.....	Yes.	
§ 63.9(i) .....	Adjustment of Deadlines .....	Yes.	
§ 63.9(j) .....	Change in Previous Information	Yes.	
§ 63.10(a) .....	Recordkeeping/Reporting—Applicability.	Yes.	
§ 63.10(b) .....	General Recordkeeping Requirements.	Yes .....	§ 63.2998 includes additional requirements.
§ 63.10(c)(1) .....	Additional CMS Recordkeeping	Yes.	
§ 63.10(c)(2)–(4) .....	.....	No .....	[Reserved].
§ 63.10(c)(5)–(8) .....	.....	Yes.	
§ 63.10(c)(9) .....	.....	No .....	[Reserved].
§ 63.10(c)(10)–(15) .....	.....	Yes.	
§ 63.10(d)(1) .....	General Reporting Requirements	Yes .....	§ 63.3000 includes additional requirements.
§ 63.10(d)(2) .....	Performance Test Results .....	Yes .....	§ 63.3000 includes additional requirements
§ 63.10(d)(3) .....	Opacity or Visible Emissions Observations.	No .....	Subpart HHHH does not specify opacity or visible emission standards.
§ 63.10(d)(4)–(5) .....	Progress Reports/Startup, Shutdown, and Malfunction Reports.	Yes.	
§ 63.10(e)(1) .....	Additional CMS Reports—General.	No .....	Subpart HHHH does not require CEMS.
§ 63.10(e)(2) .....	Reporting results of CMS performance evaluations.	Yes.	
§ 63.10(e)(3) .....	Excess Emission/CMS Performance Reports.	Yes.	
§ 63.10(e)(4) .....	COMS Data Reports .....	No .....	Subpart HHHH does not specify opacity or visible emission standards.
§ 63.10(f) .....	Recordkeeping/Reporting Waiver	Yes .....	EPA retains approval authority
§ 63.11 .....	Control Device Requirements—Applicability.	No .....	Facilities subject to subpart HHHH do not use flares as control devices.
§ 63.12 .....	State Authority and Delegations	Yes.	
§ 63.13 .....	Addresses .....	Yes.	
§ 63.14 .....	Incorporation by Reference .....	No.	
§ 63.15 .....	Availability of Information/Confidentiality.	Yes.	

APPENDIX A TO SUBPART HHHH OF  
PART 63—METHOD FOR DETERMINING  
FREE-FORMALDEHYDE IN UREA-  
FORMALDEHYDE RESINS BY SODIUM  
SULFITE (ICED & COOLED)

1.0 Scope

This procedure corresponds to the Housing and Urban Development method of determining free-formaldehyde in urea-formaldehyde resins. This method applies to samples that decompose to yield formaldehyde under the conditions of other free-formaldehyde methods. The primary use is for urea-formaldehyde resins.

2.0 Part A—Testing Resins

Formaldehyde will react with sodium sulfite to form the sulfite addition products and liberate sodium hydroxide (NaOH); however, at room temperature, the methanol groups present will also react to liberate NaOH. Titrate at 0 degrees Celsius (( °deg;C) to minimize the reaction of the methanol groups.

2.1 Apparatus Required.

2.1.1 Ice crusher.

2.1.2 One 100-milliliter (mL) graduated cylinder.

2.1.3 Three 400-mL beakers.

2.1.4 One 50-mL burette.

2.1.5 Analytical balance accurate to 0.1 milligrams (mg).

2.1.6 Magnetic stirrer.

2.1.7 Magnetic stirring bars.

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- 2.1.8 Disposable pipettes.
- 2.1.9 Several 5-ounce (oz.) plastic cups.
- 2.1.10 Ice cube trays (small cubes).
- 2.2 *Materials Required.*
- 2.2.1 Ice cubes (made with distilled water).
- 2.2.2 A solution of 1 molar (M) sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) (63 grams (g)  $\text{Na}_2\text{SO}_3$ /500 mL water ( $\text{H}_2\text{O}$ ) neutralized to thymolphthalein endpoint).
- 2.2.3 Standardized 0.1 normal (N) hydrochloric acid (HCl).
- 2.2.4 Thymolphthalein indicator (1.0 g thymolphthalein/199 g methanol).
- 2.2.5 Sodium chloride (NaCl) (reagent grade).
- 2.2.6 Sodium hydroxide (NaOH).
- 2.3 *Procedure.*
- 2.3.1 Prepare sufficient quantity of crushed ice for three determinations (two trays of cubes).
- 2.3.2 Put 70 cubic centimeters (cc) of 1 M  $\text{Na}_2\text{SO}_3$  solution into a 400-mL beaker. Begin stirring and add approximately 100 g of crushed ice and 2 g of NaCl. Maintain 0 °C during test, adding ice as necessary.
- 2.3.3 Add 10–15 drops of thymolphthalein indicator to the chilled solution. If the solution remains clear, add 0.1 N NaOH until the solution turns blue; then add 0.1 N HCl back to the colorless endpoint. If the solution turns blue upon adding the indicator, add 0.1 N HCl to the colorless endpoint.
- 2.3.4 On the analytical balance, accurately weigh the amount of resin indicated

under the “*Resin Sample Size*” chart (see below) as follows.

**RESIN SAMPLE SIZE**

Approximate free HCHO (percent)	Sample weight (gram(s))
<0.5 .....	10
0.5–1.0 .....	5
1.0–3.0 .....	2
3.0 .....	1

- 2.3.4.1 Pour about 1 inch of resin into a 5 oz. plastic cup.
- 2.3.4.2 Determine the gross weight of the cup, resin, and disposable pipette (with the narrow tip broken off) fitted with a small rubber bulb.
- 2.3.4.3 Pipette out the desired amount of resin into the stirring, chilled solution (approximately 1.5 to 2 g per pipette-full).
- 2.3.4.4 Quickly reweigh the cup, resin, and pipette with the bulb.
- 2.3.4.5 The resultant weight loss equals the grams of resin being tested.
- 2.3.5 Rapidly titrate the solution with 0.1 N HCl to the colorless endpoint described in Step 3 (2.3.3).
- 2.3.6 Repeat the test in triplicate.
- 2.4 *Calculation.*
- 2.4.1 The percent free-formaldehyde (%HCHO) is calculated as follows:

$$\% \text{HCHO} = \frac{(\text{mL } 0.1 \text{ N HCl}) (\text{N of Acid}) (3.003)}{\text{Weight of Sample}}$$

- 2.4.2 Compute the average percent free-formaldehyde of the three tests.

(NOTE: If the results of the three tests are not within a range of  $\pm 0.5$  percent or if the average of the three tests does not meet expected limits, carry out Part B and then repeat Part A.)

**3.0 Part B—Standard Check**

Part B ensures that test reagents used in determining percent free-formaldehyde in urea-formaldehyde resins are of proper concentration and that operator technique is correct. Should any doubts arise in either of these areas, the formaldehyde standard solution test should be carried out.

**3.1 Preparation and Standardization of a 1 Percent Formalin Solution.**

Prepare a solution containing approximately 1 percent formaldehyde from a stock 37 percent formalin solution. Standardize the prepared solution by titrating the hydroxyl ions resulting from the formation of the formaldehyde bisulfite complex.

**3.2 Apparatus Required.**

NOTE: All reagents must be American Chemical Society analytical reagent grade or better.

- 3.2.1 One 1-liter (L) volumetric flask (class A).
- 3.2.2 One 250-mL volumetric flask (class A).
- 3.2.3 One 250-mL beaker.
- 3.2.4 One 100-mL pipette (class A).
- 3.2.5 One 10-mL pipette (class A).
- 3.2.6 One 50-mL graduated cylinder (class A).
- 3.2.7 A pH meter, standardized using pH 7 and pH 10 buffers.
- 3.2.8 Magnetic stirrer.
- 3.2.9 Magnetic stirring bars.
- 3.2.10 Several 5-oz. plastic cups.
- 3.2.11 Disposal pipettes.
- 3.2.12 Ice cube trays (small cubes).
- 3.3 *Materials Required.*
- 3.3.1 A solution of 37 percent formalin.
- 3.3.2 Anhydrous  $\text{Na}_2\text{SO}_3$ .
- 3.3.3 Distilled water.

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3.3.4 Standardized 0.100 N HCl.

3.3.5 Thymolphthalein indicator (1.0 g thymolphthalein/199 g methanol).

3.4 *Preparation of Solutions and Reagents.*

3.4.1 Formaldehyde Standard Solution (approximately 1 percent). Measure, using a graduated cylinder, 27.0 mL of analytical reagent 37 percent formalin solution into a 1-L volumetric flask. Fill the flask to volume with distilled water.

(NOTE: You must standardize this solution as described in section 3.5. This solution is stable for 3 months.)

3.4.2 Sodium Sulfite Solution 1.0 M (used for standardization of Formaldehyde Standard Solution). Quantitatively transfer, using distilled water as the transfer solvent, 31.50 g of anhydrous  $\text{Na}_2\text{SO}_3$  into a 250-mL volumetric flask. Dissolve in approximately 100 mL of distilled water and fill to volume.

(NOTE: You must prepare this solution daily, but the calibration of the Formaldehyde Standard Solution needs to be done only once.)

3.4.3 Hydrochloric Acid Standard Solution 0.100 M. This reagent should be readily available as a primary standard that only needs to be diluted.

3.5 *Standardization.*

3.5.1 Standardization of Formaldehyde Standard Solution.

3.5.1.1 Pipette 100.0 mL of 1 M sodium sulfite into a stirred 250-mL beaker.

3.5.1.2 Using a standardized pH meter, measure and record the pH. The pH should be around 10. It is not essential the pH be 10; however, it is essential that the value be accurately recorded.

3.5.1.3 To the stirring  $\text{Na}_2\text{SO}_3$  solution, pipette in 10.0 mL of Formaldehyde Standard Solution. The pH should rise sharply to about 12.

3.5.1.4 Using the pH meter as a continuous monitor, titrate the solution back to the original exact pH using 0.100 N HCl. Record the milliliters of HCl used as titrant. (NOTE: Approximately 30 to 35 mL of HCl will be required.)

3.5.1.5 Calculate the concentration of the Formaldehyde Standard Solution using the equation as follows:

$$\% \text{HCHO} = \frac{(\text{mL } 0.1 \text{ N HCl})(\text{N Acid})(3.003)}{\text{Weight of Formaldehyde Standard Solution}}$$

3.7.2 The range of the results of three tests should be no more than  $\pm 5$  percent of the actual Formaldehyde Standard Solution concentration. Report results to two decimal places.

3.8 *Reference.*

$$\% \text{HCHO} = \frac{(\text{mL HCl})(\text{N HCl})(3.003)}{\text{mL sample}}$$

3.6 *Procedure.*

3.6.1 Prepare a sufficient quantity of crushed ice for three determinations (two trays of cubes).

3.6.2 Put 70 cc of 1 M  $\text{Na}_2\text{SO}_3$  solution into a 400-mL beaker. Begin stirring and add approximately 100 g of crushed ice and 2 g NaCl. Maintain 0 °C during the test, adding ice as necessary.

3.6.3 Add 10–15 drops of thymolphthalein indicator to the chilled solution. If the solution remains clear, add 0.1 N NaOH until the solution turns blue; then add 0.1 N HCl back to the colorless endpoint. If the solution turns blue upon adding the indicator, add 0.1 N HCl to the colorless endpoint.

3.6.4 On the analytical balance, accurately weigh a sample of Formaldehyde Standard Solution as follows.

3.6.4.1 Pour about 0.5 inches of Formaldehyde Standard Solution into a 5-oz. plastic cup.

3.6.4.2 Determine the gross weight of the cup, Formaldehyde Standard Solution, and a disposable pipette fitted with a small rubber bulb.

3.6.4.3 Pipette approximately 5 g of the Formaldehyde Standard Solution into the stirring, chilled  $\text{Na}_2\text{SO}_3$  solution.

3.6.4.4 Quickly reweigh the cup, Formaldehyde Standard Solution, and pipette with the bulb.

3.6.4.5 The resultant weight loss equals the grams of Formaldehyde Standard Solution being tested.

3.6.5 Rapidly titrate the solution with 0.1 N HCl to the colorless endpoint in Step 3 (3.6.3).

3.6.6 Repeat the test in triplicate.

3.7 *Calculation for Formaldehyde Standard Solution.*

3.7.1 The percent free-formaldehyde (% HCHO) is calculated as follows:

West Coast Adhesive Manufacturers Trade Association Test 10.1.